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SPECIFICATION

METHODS FOR IMPROVING DISCOLORATION IN PULPS
AND PULPS WITH IMPROVED DISCOLORATION

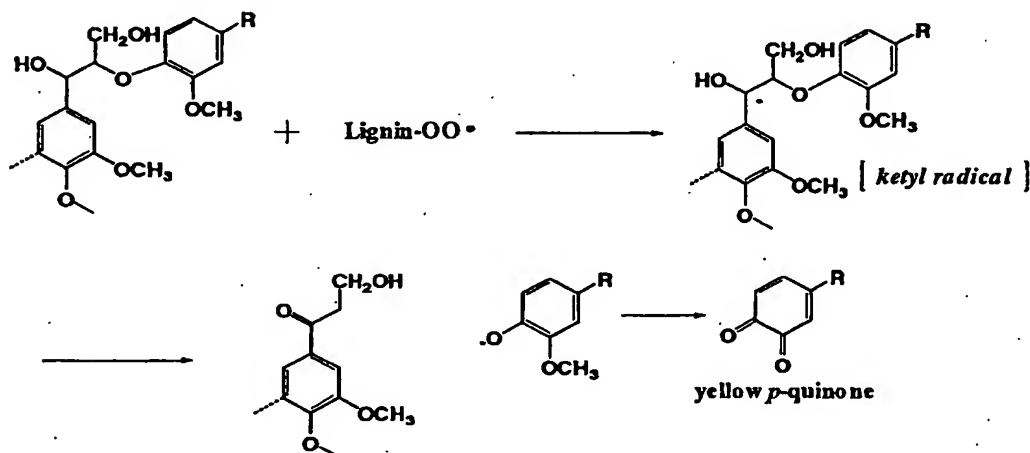
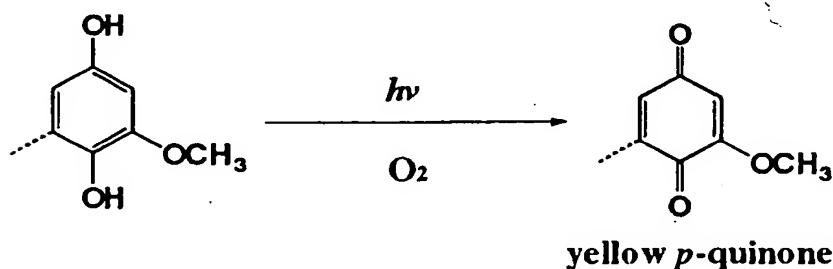
5 TECHNICAL FIELD

The present invention relates to methods for improving discoloration in pulp, more specifically to novel methods for improving discoloration in pulp using specific compounds, and to pulp with improved discoloration prepared by the methods for improving discoloration.

PRIOR ART

Brightness loss or discoloration in pulp over time is a common issue for any type of pulp including chemical pulp (hereinafter referred to as CP) such as KP, AP, SP; semi-chemical pulp (hereinafter referred to as SCP); mechanical pulp (hereinafter referred to as MP) such as SGP, RGP, PGW, TMP, CTMP, BCTMP; and deinked pulp (hereinafter referred to as DIP). The extent of discoloration in pulp is mainly influenced by the residual amount of lignin or modified lignin in the pulp, and discoloration tends to advance as the residual amount of lignin or modified lignin increases. Thus, discoloration advances the most rapidly in MP characterized by low degrees of bleaching, followed by SCP, and then CPs. Discoloration in DIP is greatly influenced by the MP content or other factors.

During bleaching of pulp, lignin is oxidized to produce a hydroquinone as modified lignin. This hydroquinone is readily oxidized via the reaction shown in Scheme 1 to give a quinone, resulting in coloration. The lignin remaining unoxidized in the pulp is also excited with UV light and oxidatively degraded via the reaction shown in Scheme 2 to freshly produce a quinone compound, resulting in coloration. Thus, conventional methods for improving discoloration in pulp normally comprise degrading or removing causative agents of discoloration such as lignin or modified lignin by adding bleaching chemicals or alkaline chemicals during the pulp bleaching process.



According to a conventional method for improving discoloration in CP, causative agents of discoloration such as lignin or hexenuronic acid are degraded and removed with chemicals or the like. In this method, 5 however, large amounts of chemicals or the like must be used to degrade/remove lignin and these treatments cause problems such as yield losses in bleached pulp or strength losses in pulp fibers. Large amounts of acids are required to remove hexenuronic acid, which also invites 10 the problem of strength losses in pulp fibers. If the quinone compound could be degraded in advance, such benefits as quality stabilization of paper products made from CP and the possibility of the development of new products would be expected.

15 As an example of prior art, a document shows that discoloration is improved better at higher temperatures with higher hydrogen peroxide concentrations for longer reaction periods during the hydrogen peroxide-bleaching stage under alkaline conditions (see non-patent document 20 1). A bleaching process has been patented, characterized in that an alkali is added late in the first reaction of successive chlorine dioxide stages when a pulp derived from a lignocellulose material is bleached through a bleaching sequence consisting of chlorine and/or chlorine 25 dioxide stage - alkali/oxygen stage -chlorine dioxide stage -chlorine dioxide stage and that the ratio of chlorine dioxide at the first to second stages is 40/60 to 70/30 (see patent document 1). A multi-stage bleaching

process has also been patented, comprising the step of treating a pulp derived from a lignocellulose material with chlorine, alkaline extraction, and then a hypochlorite, characterized in that 1.0% or more of an alkali is added on the basis of the bone dry weight of the pulp during the hypochlorite-bleaching stage and the pulp is treated at a temperature of 60°C or more (see patent document 2). A technique has been disclosed, which is characterized in that a pulp bleached in a sequence including at least one chlorine bleaching stage is treated with xylanase and further bleached in a bleaching sequence including a hypochlorite stage and a chlorine dioxide stage (see patent document 3). A process for preparing a pulp with high brightness has been disclosed, comprising further bleaching a bleached pulp derived from a lignocellulose material through a sequence of a hyposulfite bleaching stage under high temperature and high alkali conditions and a chlorine dioxide bleaching stage, wherein the second chlorine dioxide bleaching stage is performed at a chlorine dioxide concentration of 1% by weight to 3% by weight on the basis of the bone dry weight of the pulp in a chlorine dioxide/alkali ratio of 1/0.05 to 1/0.3 and at a high temperature (see patent document 4).

It has become known from recent findings that not only conventional lignin and modified lignin but also hexenuronic acid are responsible for discoloration in ECF or TCF bleached pulp. This hexenuronic acid is produced by demethylation from methylglucuronic acid in

hemicellulose during a cooking step. This hexenuronic acid is said to be responsible for discoloration in pulp. An acid treatment at a relatively high temperature was proposed to remove the hexenuronic acid. According to
5 this method, the hexenuronic acid and modified lignin are removed by acid hydrolysis by treating unbleached pulp at high temperatures under acid conditions. For example, a technique has been disclosed wherein a suspension of a cellulose pulp prepared by the sulfate process or alkaline
10 process is heated and treated at about 85 to 150°C and a pH of about 2 to 5 to remove at least about 50% of hexenuronic acid in the cellulose pulp, thereby decreasing the Kappa number of the pulp by 2 to 9 units (see patent document 5).

15 MP have a pulp yield reaching even 90 to 95% because they are prepared by grinding wood chips into fibers. Thus, it would be desirable to expand the use of MP for the purpose of effective utilization of forest resources. However, MP are mainly used for mechanical paper and
20 newsprint papers due to the problem of significant discoloration, and are only partially used for applications requiring high brightness and long shelf life such as printing paper and recording paper at present. The mechanism of discoloration in MP is the same as that
25 of the lignin-induced discoloration in the pulp described above, but discoloration in MP is more severe than in CP and SCP because of the higher residual amount of lignin and modified lignin than in CP and SCP. A major cause of

the strong coloration in MP is that lignin is oxidized during hydrogen peroxide-bleaching to produce a hydroquinone, which is readily oxidized into a quinone. Discoloration becomes more severe in MP having higher
5 brightness because more hydroquinone is produced at higher degrees of bleaching. The lignin remaining unoxidized in MP is also excited with UV light and oxidatively degraded to newly produce a quinone compound, resulting in coloration. Thus, the main factor of the severe
10 discoloration in MP is the quinone compound, and if this quinone compound could be degraded in advance, the severe discoloration in MP would be greatly reduced and many benefits would be expected such as (1) quality stabilization of current paper products containing MP, (2)
15 enrichment in MP in current paper products with limited content of MP due to the discoloration in MP, (3) the possibility of the development of new products containing MP, etc.

To solve the problem of the discoloration in MP,
20 many proposals have been made over a long period of time, and a method using, for example, a water-soluble UV absorbent and a photostabilizer in combination has been recently shown (see non-patent document 2). A method in which the aromatic ring contained in the lignin in MP is
25 reduced was also shown (see non-patent document 3).

However, UV absorbents or the like have a disadvantage in that their effect does not continue for a long period because they are deteriorated by UV light. On the other

hand, when a rhodium catalyst was used for reducing the lignin aromatic ring, it took such a long period as 5 days to partially hydrogenate the aromatic ring in the hydrogenation reaction of the aromatic ring of the lignin isolated from wood at room temperature in an aqueous alcohol solution, and this catalyst seems very difficult to directly react with the lignin present in pulp fibers because it is used as an emulsion. Thus, all of these conventional methods have disadvantages such as insufficient anti-fading effect, long processing time, lack of economy or practicability, etc. at present.

One of the applicants of the present invention, the National Institute of Advanced Industrial Science and Technology, has already filed three applications for pulp bleaching methods involving irradiation with UV and/or visible light. Specifically, a technique is disclosed involving irradiation with UV and/or visible light in bleaching pulp using a reducing agent (see patent document 6). Another technique is disclosed involving irradiation with UV and/or visible light in the presence of an organic peroxide represented by ROOR' as an oxidizing agent (see patent document 7). Still another technique is disclosed combining the use of hydrogen peroxide and UV and/or visible light (see patent document 8). The present invention provides methods for improving discoloration in pulp by applying the techniques of these prior inventions to bleached pulp.

Non-patent and patent documents cited herein as

prior art are as follows:

The Bleaching of Pulp, P382, P384, TAPPI PRESS
(1979), N. Hartler, TAPPI 43 (11) 903 (1960) (non-patent
document 1); Japanese Patent No. 1983064 (patent document
5 1); Japanese Patent No. 2115315 (patent document 2); JPA
HEI 6-101185 (patent document 3); JPA HEI 9-105091 (patent
document 4); JPA HEI 10-508346 (patent document 5); Yuan,
Z., et al., J. Pulp Paper Sci., 28 (5), 159 (2002) (non-
patent document 2); Hu, T. Q., et al., J. Pulp Paper Sci.,
10 25 (9), 312 (1999) (non-patent document 3); JPA 2002-88671
(patent document 6); JPA 2002-88672 (patent document 7);
JPA 2002-88673 (patent document 8).

DISCLOSURE OF THE INVENTION

15 The present invention aims to provide a method for
improving discoloration in pulp, characterized by:

- (1) a versatile technique adaptable to any type of
pulp;
- (2) a time-saving process;
- 20 (3) a great and permanent anti-fading effect;
- (4) environmental friendliness without unpleasant
odor or toxicity;

and other properties, as well as a pulp with greatly
improved discoloration obtained by said method for
25 improving discoloration.

Discoloration in pulp can be greatly improved by
adding one or more additives selected from the group
consisting of reducing agents, peroxides and hydrogen-

donating organic compounds to one of bleached CP, SCP, MP and DIP or a mixture of two or more of them and irradiating it with UV and/or visible light.

5 BRIEF EXPLANATION OF THE DRAWINGS

FIG. 1 is a graph showing the anti-fading effect based on the brightness depending on the laser irradiation time.

FIG. 2 is a graph showing the anti-fading effect
10 based on the brightness depending on the laser wavelength.

FIG. 3 is a graph showing the anti-fading effect based on the L*a*b* color difference depending on the laser irradiation time.

FIG. 4 is a graph showing the anti-fading effect
15 based on the L*a*b* color difference depending on the laser wavelength.

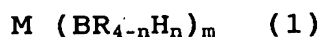
PREFERRED EMBODIMENTS OF THE INVENTION

Pulp suitable for improving discoloration according
20 to the present invention includes common bleached CP, SCP, MP and DIP derived from wood. Any one of these pulp or a mixture of two or more of the pulp may be used. The term "bleached" here means that a CP, for example, has gone through a normal multi-stage bleaching or short sequence
25 bleaching process.

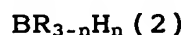
Specific compounds that can be used in the present invention include known reducing agents, peroxides and hydrogen-donating organic compounds used as

bleaching/decoloring agents. Pulp is treated in the presence of at least one compound among these groups.

Such reducing agents include, for example, sulfite or bisulfite ion, hydrosulfites, boron hydride compounds, etc. The boron hydride compounds are normally represented by general formula (1) or (2) below.



wherein n = an integer of 1 to 4, m = an integer of 1 to 3, M = a metal ion, organic ion or inorganic ion, R = a hydrocarbon group or substituted hydrocarbon group or



wherein n = an integer of 1 to 3, R = a hydrocarbon group or substituted hydrocarbon group.

In general formula (1) above, the metal ion is intended to include monovalent metal ions such as alkali metals, divalent metal ions such as alkali earth metals, and trivalent metal ions; and the organic ion may be any stable one, especially a quaternary ammonium ion.

Substituents for R include aliphatic hydrocarbon groups preferably containing 1 to 20, more preferably 1 to 10 carbon atoms, aromatic hydrocarbon groups preferably containing 6 to 20, more preferably 6 to 14 carbon atoms, substituted hydrocarbon groups preferably containing 7 to 40, more preferably 7 to 24 carbon atoms, etc. When two or more substituents for R exist, R may be the same or different. Especially preferred boron hydride compounds for use in the present invention are sodium borohydride and tetrabutylammonium borohydride.

As for peroxides, both organic peroxides and inorganic peroxides can be used. Organic peroxides that can be used are compounds represented by general formula (3) below:



wherein R and R' may be the same or different and represent a hydrocarbon group, alkylcarbonyl group, arylcarbonyl group, alkoxycarbonyl group, aryloxy carbonyl group, formyl group or hydrogen.

10 Hydrocarbon groups include aromatic hydrocarbon groups such as phenyl, naphthyl, biphenyl and anthryl groups; aliphatic hydrocarbon groups; and substituted forms thereof; alkylcarbonyl groups include acetyl, ethylcarbonyl and propionylcarbonyl groups and substituted
15 forms thereof; arylcarbonyl groups include benzoyl, naphthylcarbonyl and biphenylcarbonyl groups and substituted forms thereof; alkoxycarbonyl groups include methoxycarbonyl and ethoxycarbonyl groups and substituted forms thereof; and aryloxy carbonyl groups include
20 phenoxycarbonyl, naphthoxycarbonyl and biphenyloxycarbonyl groups and substituted forms thereof. R and R' may be the same or different. Specific examples of these organic peroxides include, for example, peracids such as perbenzoic acid and derivatives thereof, peracetic acid
25 and performic acid; esters of these peracids; and percarbonic acid and esters thereof. Inorganic peroxides include hydrogen peroxide, sodium peroxide, etc.

Hydrogen-donating organic compounds are preferably

primary alcohols represented by general formula (4) below, and specifically include ethyl alcohol, benzyl alcohol, furfuryl alcohol, etc.



5 wherein R represents an alkyl, aryl, etc.

In the present invention, the reducing agents, peroxides and hydrogen-donating organic compounds may be used alone in the absence of a solvent, but should desirably be used as a dispersion or solution in a solvent
10 transparent to UV and/or visible light. Such solvents include water, alcohols, linear or cyclic alkanes, ethers, etc. alone or mixtures thereof, preferably water.

The amount of any of the reducing agents, peroxides and hydrogen-donating organic compounds used is not
15 specifically limited so far as it is at or below the saturated concentration of the compound in the solvent, but preferably 0.01 to 40% (weight/volume), more preferably 0.1 to 20% in the solvent. The amount of any of the reducing agents, peroxides and hydrogen-donating
20 organic compounds used is 0.05 to 50% solids by weight, more preferably 0.1 to 25% solids by weight on the basis of pulp solids.

The UV and/or visible light is not specifically limited, but is desirably used at a wavelength of about
25 180 to 800 nm, preferably 200 to 500 nm. This is because lignin, para-quinone and ortho-quinone have maximum absorption wavelengths of 280 nm, 360 nm and 390 to 410 nm, respectively. Suitable light sources include common light

sources such as low-pressure mercury lamps, high-pressure mercury lamps and xenon lamps; and various excimer lamps and various lasers; but it is desirable to use laser light sources in view of high-speed processing. The laser light
5 sources are not specifically limited and the laser light may be pulsed or continuous, but it is preferable to use excimer lasers (ArF excimer laser, KrF excimer laser, XeCl excimer laser, XeF excimer laser, etc.), argon ion laser, krypton ion laser, the second and third harmonics of YAG
10 lasers, etc.

The irradiation intensity is not specifically limited, but is suitably $0.1 \text{ mJ/cm}^2/\text{pulse}$ to $1.0 \text{ kJ/cm}^2/\text{pulse}$ for pulsed radiation and 0.1 mW to 10 kW/cm^2 for continuous radiation. The irradiation temperature is
15 not specifically limited either, but is preferably -80 to 100°C , more preferably 0 to 80°C . The irradiation time is appropriately determined taking into account the masses of potential coloring materials contained in raw pulps, the types and concentrations of additives or solvents, and the
20 type and intensity of the irradiating UV and/or visible light, but normally 1 to 60 minutes will suffice.

The present invention is not specifically limited to any embodiment provided that (1) a bleached pulp is brought into contact with (2) at least one compound
25 selected from reducing agents, peroxides and hydrogen-donating organic compounds and irradiated with (3) UV and/or visible light. According to a preferred embodiment, for example, (1) a raw pulp is dispersed in a solvent

containing (2) at least one compound selected from reducing agents, peroxides and hydrogen-donating organic compounds and transparent to UV and/or visible light and then irradiated with (3) UV and/or visible light.

5 Specifically when the solvent is water, the aqueous suspension of pulp having gone through bleaching and issuing from the bleaching step is combined and mixed with at least one compound selected from reducing agents, peroxides and hydrogen-donating organic compounds and then
10 irradiated with UV and/or visible light. Alternatively, (1) a raw pulp is formed into a sheet or thin layer, which is then impregnated with a solvent containing (2) at least one compound selected from reducing agents, peroxides and hydrogen-donating organic compounds, and then irradiated
15 with (3) UV and/or visible light. Specifically when the solvent is water, the aqueous suspension of pulp having gone through bleaching and issuing from the bleaching step is dewatered through an apparatus such as a pulp sheet machine into a pulp sheet, which is then impregnated with
20 at least one compound selected from reducing agents, peroxides and hydrogen-donating organic compounds and irradiated with UV and/or visible light.

Although the anti-fading mechanism according to the present invention is not known in detail, we assume as
25 follows. That is, potential coloring materials contained in pulp, such as lignin in MP, are oxidatively degraded by irradiation with UV and/or visible light during bleaching to produce a hydroquinone according to the present

invention. Unmodified lignin remaining unoxidized during bleaching produces various quinones. The present invention takes advantage of the phenomenon in which these quinones are electronically excited from the ground state into the excited state by UV and/or visible light, and as a result, converted into a state having more active substances, thereby enhancing the reaction with the coexisting at least one compound selected from reducing agents, peroxides and hydrogen-donating organic compounds to promote the degradation reaction of the coloring materials or the hydrogenation reaction of double bonds, or conversely the phenomenon in which at least one compound selected from reducing agents, peroxides and hydrogen-donating organic compounds is converted into a more active substance by irradiation with UV and/or visible light, thereby improving the reactivity with the coloring materials to enhance the degradation reaction of the coloring materials or the hydrogenation reaction of double bonds.

In contrast to the method previously proposed as a method for controlling discoloration by incorporating an additive such as a thiol compound into a paper made from an MP, which was associated with unpleasant odor and high toxicity and did not lead to a radical improvement because such a method merely promoted the reaction of quinones into hydroquinones and discoloration recurred by UV light once the additive had been consumed, the method for improving discoloration according to the present invention

not only completely resolves all these problems by adopting a unique means, i.e. irradiation with UV and/or visible light in the presence of at least one compound selected from reducing agents, peroxides and hydrogen-
5 donating organic compounds, but also has a remarkable advantage in environmental friendliness.

EXAMPLES

The following examples further illustrate the
10 present invention in detail without, however, limiting the invention thereto.

[Example 1]

A hand-made paper containing a bleached MP and a
15 bleached CP made from coniferous wood in a ratio of 1:1 (200 cm², basis weight 60 g/m²) was divided into four portions to prepare samples for laser processing. These samples were immersed in a 6% aqueous sodium borohydride (w/v) solution and then mounted on a glass plate. At this
20 point, the impregnation level of sodium boron hydride was 18% solids by weight on the basis of the weight of pulp solids. The samples were irradiated with KrF excimer laser at 40 mJ/cm²/pulse, 5 Hz for 10 minutes. After completion of laser irradiation, the sample was washed
25 with water and dried in a cylinder dryer. A fading test was performed using a xenon lamp weather meter. The samples were irradiated with UV light generated from the xenon lamp for 0.5, 1.0, and 2.0 hours, after which ISO

brightness [JIS 8148] and L*a*b* color difference (ΔE^*_{ab}) [JIS Z 8701] were determined. The fading test was performed at a black panel temperature of 63°C, humidity 50%, and an irradiation intensity of 70 W.

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[Example 2]

The same procedure as in Example 1 was performed except that the irradiation time of KrF excimer laser was changed to 20 minutes.

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[Example 3]

The same procedure as in Example 1 was performed except that the irradiation time of KrF excimer laser was changed to 40 minutes.

15

[Example 4]

The same procedure as in Example 2 was performed except that XeCl excimer laser was used in place of KrF excimer laser.

20

[Comparative example 1]

The samples for laser processing in Example 1 were immersed in water and then dried in a cylinder dryer and subjected to the fading test.

25

[Comparative example 2]

The same procedure as in Example 2 was performed except that the samples were allowed to stand for 20

minutes on the glass plate without laser irradiation.

The results were shown in Figures 1 to 4.

[Example 1]

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bleached CP made from coniferous wood in a ratio of 1:1
(200 cm², basis weight 60 g/m²) was divided into four
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performed at a black panel temperature of 63°C, humidity
50%, and an irradiation intensity of 70 W.

25 [Example 2]

The same procedure as in Example 1 was performed
except that the irradiation time of KrF excimer laser was
changed to 20 minutes.

[Example 3]

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[Example 4]

The same procedure as in Example 2 was performed except that XeCl excimer laser was used in place of KrF excimer laser.

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[Comparative example 1]

The samples for laser processing in Example 1 were immersed in water and then dried in a cylinder dryer and subjected to the fading test.

15

[Comparative example 2]

The same procedure as in Example 2 was performed except that the samples were allowed to stand for 20 minutes on the glass plate without laser irradiation.

20

The results were shown in Figures 1 to 4.

It was shown that when an MP was irradiated with KrF excimer laser, the discoloration tendency decreased as the irradiation time increased (Figures 1, 3). Especially, the samples irradiated with the laser for 40 minutes showed very little discoloration and a significant brightness difference of 16 points compared with blanks after the fading test for 2 hours. As a result of the comparison between the anti-fading effects of KrF excimer

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laser and XeCl excimer laser, very little difference was observed between them (Figures 2, 4).

ADVANTAGES OF THE INVENTION

5 Any type of pulp can be treated rapidly to produce a great and permanent anti-fading effect as well as other advantages such as environmental friendliness by providing a novel method for improving discoloration in pulp comprising irradiating a pulp with UV and/or visible light
10 in the presence of at least one compound selected from the group consisting of reducing agents, peroxides and hydrogen-donating organic compounds. Moreover, pulp with greatly improved discoloration obtained by the present method for improving discoloration can be used as raw
15 materials to produce further benefits such as quality stabilization of paper products, development of new products, expanded applications of MP, etc.